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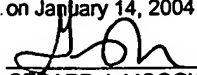
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PATENT
#02-0548-UNI
Case #F3318(C)



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Ormerod et al.
Serial No.: 10/678,465
Filed: October 3, 2003
For: Freezing Vegetables

Edgewater, New Jersey 07020
January 14, 2004

SUBMISSION OF PRIORITY DOCUMENT

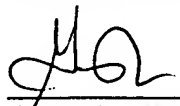
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Washington, D.C. 20231

Sir:

Pursuant to rule 55(b) of the Rules of Practice in Patent Cases, Applicant(s) is/are submitting herewith a certified copy of the United Kingdom Application No. 0223339.3 filed October 8, 2002, upon which the claim for priority under 35 U.S.C. § 119 was made in the United States.

It is respectfully requested that the priority document be made part of the file history.

Respectfully submitted,



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INVESTOR IN PEOPLE

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1/77
09 OCT 02 E754 65-4 C03008
P01/7700 0.00-0223339.3

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1. Your reference	PB - F3318		
2. Patent application number (The Patent Office will fill in this part)	0223339.3		08 OCT 2002
3. Full name, address and postcode of the or of each applicant (underline all surnames)	UNILEVER PLC Unilever House, Blackfriars, London, EC4P 4BQ		
Patents ADP number (if you know it)	1628002		
If the applicant is a corporate body, give the country/state of its incorporation	Great Britain		
4. Title of the invention	FREEZING VEGETABLES		
5. Name of your agent (if you have one)	Lloyd Wise		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	Commonwealth House, 1 - 19 New Oxford Street, London, WC1A 1LW		
Patents ADP number (if you know it)	117001		
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11. I/We request the grant of a patent on the basis of this application.

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8th October 2002

LLOYD WISE

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DUPLICATE

F3318

1

Freezing vegetables

Field of the invention

5 The invention relates to a process for freezing vegetables and the frozen vegetables provided thereby. More particularly the invention relates to a freezing process which provides frozen vegetables of excellent quality when defrosted for consumption.

10

Background to the invention

Various attempts have been in the art to improve the quality of vegetables which have been stored frozen by way of the
15 freezing process applied.

US patent 3,736,154 describes a process of ultraslow freezing which discloses the maintenance of intact cell membranes in the product by way of a freezing regime with a
20 cooling rate of about 0.1 to 0.3°C per hour. This process is disclosed as achieving dehydration of the inner cell as water within the cell moves outside the cell membrane where it freezes without the destruction of the cell membrane.

25 Unfortunately this process is not a viable approach to the commercial preparation of frozen vegetables. Not only does this process not tolerate a blanching step which is necessary as a microbiological and enzyme deactivation step in modern vegetable processing, but also this process takes
30 several days to complete.

US 6 096 361 discloses a similar method of preservation wherein food is relatively rapidly cooled from room temperature to close to the freezing point and then slowly cooled at a gradual cooling rate of 0.01 to 0.5°C/hour to
5 below the freezing point. This non-frozen preservation method may be then followed by a rapid freezing treatment to achieve a food wherein the outer cells of the food are frozen and the inner cell preserved in a non-frozen state. It is disclosed that free water moves from the intracellular
10 fluid to the extra cellular fluid, resulting in the simultaneous dilution of the extra cellular fluid and concentration of the intracellular fluid, which makes it easier for the extra cellular fluid to freeze and, conversely, more difficult for the intracellular fluid to
15 freeze.

An alternative freezing process of the prior art for improving frozen vegetable quality is described in European Patent 0 554 468 B1 in which potatoes are cooked and frozen.
20 Freezing is described as a 2 step process wherein, in a initial step, the core of the potatoes is kept at the crystallisation stage of water for a period of 15 to 60 minutes. In a second step deep-freezing is continued until a storage temperature of -20°C.

25

Our European Patent Application No. 02251681 discloses a process for the production of a frozen vegetable or part thereof, wherein said process comprises the steps:

- (i) heat treating a vegetable or part thereof;
- 30 (ii) under-cooling to a maximum core temperature of less than or equal to -5°C;

(iii) reducing the core temperature to less than or equal to -18°C ;

5 The process produces a frozen vegetable or part thereof comprising a core ice content, in which at least 40% of said core ice content is located within a plurality of cellular structures, wherein the perimeter of each cellular structure is defined by a cell wall. The freezing process can practically eliminate ice formation outside the cell wall of
10 the vegetable tissue and so provide a texture, appearance and thus product quality that was not previously possible in frozen vegetables.

15 Under-cooling refers to the reduction of the temperature of the vegetable or part thereof to a temperature below the freezing point (i.e., the temperature at which freezing is possible) without the formation of ice crystals occurring.

20 The core refers to that part of the vegetable or part thereof which is at least 5mm from the external air contact surface. Preferably the core refers to that part of the vegetable or part thereof which is at least 10mm from the external air contact surface, most preferably at least 15mm therefrom.

25 Extra-cellular ice is an expression used to define ice formed outside the confines of cellular structures, wherein the perimeter of each cellular structure is defined by a cell wall. It therefore follows that intra-cellular ice
30 refers to ice formed within the confines of said cellular structures i.e. within the confines of a cell wall.

Core ice content and the proportion thereof that is intra-cellular or extra-cellular in its formation is determined by the following method using low temperature scanning electron microscopy.

5

Vegetable samples sealed in polythene bags and having been stored at -80°C and kept cold during analysis by transferring them to the Scanning electron microscopy laboratory in an insulated box containing carbon dioxide.

10

5mm x 5mm x 10mm sub-samples were cut from the chosen vegetable using a liquid nitrogen pre-cooled scalpel blade wherein cutting was carried out on an aluminium plate sitting on a bed of solid carbon dioxide to maintain sample temperature.

15

These sub-samples were mounted on to a 7mm conical depression in a 10mm diameter aluminium scanning electron microscope stub using Tissue-Tek compound (available from Sakura and comprising <11% polyvinyl alcohol, <5% carbowax and at least 85% non-reactive ingredients). at the point of freezing and immediately plunged in to nitrogen slush. The stub and sub-sample was mounted on a holder and transferred to an Oxford Instruments CP2000 low temperature preparation chamber pumped with an Edwards 306 vacuum station (5×10^{-7} Torr) via an airlock. The sample was allowed to warm to -95°C and then fractured using the point of a scalpel blade. After etching the ice for 5 minutes the sample was cooled to -110°C and coated with Gold/ Palladium (6mA, 6×10^{-1} mBar Argon, 20 seconds). The vacuum was allowed to recover to 5×10^{-7} Torr and the sample transferred to a Cressington Instruments cold stage in a JEOL 6301F Low Temperature Field

25

30

Emission Scanning Electron Microscope using an airlock transfer device.

Samples were examined at -150°C and ice was identified as
5 etched depressions in the fracture surface topography. Images of the intra and extracellular ice were recorded digitally at $\times 100$ and these images then quantified using a Zeiss (Imaging Associates) KS 400 Image Analysis system. Intracellular and extracellular ice content for the core
10 refers to a % of the total ice observed in an image as being located within and outside the cell walls respectively.

The heat treatment step disclosed in European Patent Application No. 02251681 is said to be sufficient to destroy
15 the cell membranes within the vegetable material and by so doing provides a uniform solute concentration across the tissues as free diffusion equilibrates solute levels. This is a necessary precursor to subsequent cooling steps in the process as any variation in solute concentration will give
20 rise to relative variation in the temperature at which freezing will occur and thereby reduce the ability to achieve effective under-cooling.

It is stated the heat treatment of vegetables can also
25 perform a number of other functions by providing pasteurisation of the vegetable material and deactivation of enzymes that accelerate vegetable spoilage such as lipooxygenases.

30 Preferably heat treatment is undertaken by blanching as this results in the destruction of cell membranes and the

inactivation of some or all of the endogenous enzymes present.

It has now been found that if the heat treatment step is replaced by the firming treatment there is a significant improvement in the cooked texture of the vegetables compared to vegetables subjected to conventional commercial freezing methods.

10 Summary of the Invention

Accordingly, there is provided a process for the production of a frozen vegetable or part thereof, wherein said process comprises the steps:

15

(i) subjecting a vegetable or part thereof to a firming treatment selected from:

a) immersing the vegetable or part thereof in a solution of a calcium salt.

20

b) heating the vegetable or part thereof to a temperature in the range 50 to 70°C, and

c) a combination of a) and b);

25

(ii) under-cooling to a core temperature of less than or equal to -5°C;

(iii) reducing the temperature to less than or equal to -18°C.

30

The process of the present invention provides high quality frozen vegetables to the consumer, and more particularly provides frozen vegetables which, when thawed, give rise to

a product texture and appearance which closely resembles that of fresh vegetables.

5 The addition of calcium to vegetables is known to limit the softening that vegetables undergo on subsequent higher temperature heating, such as canning or cooking. However, the quality benefits of the calcium addition prior to conventional freezing is somewhat limited. Surprisingly the combination of calcium addition and the controlled freezing
10 regime according to the invention provides a significant improvement.

Pectin is a key component of the cell walls of vegetables and fruits and exists in the form of a gel network. The
15 pectin in the middle lamellae between the primary cell walls of adjacent cells essentially acts as an adhesive between the cells, whilst the pectin matrix within the primary cell wall itself is believed to control the porosity. Enzymes present within the tissue can act on the pectin causing it
20 to change its structure and properties. For example, pectin methyl esterase can de-esterify pectin. The presence or addition of calcium can then lead to cross-links being formed between pectin molecules, which can strengthen the pectin network. This change in the structure and properties
25 of the pectin gel can produce different tissue properties, for example it reduces the softening of the tissue on heating, by limiting the loss in cell adhesion.

Suitable calcium salts include calcium sulphate, calcium
30 chloride, calcium citrate, monocalcium phosphate and mixtures thereof. The salts are employed in aqueous solution generally at a concentration of from 0.1 to 10%

calcium e.g. 1% calcium. The vegetables or vegetable portions are immersed in the solution, generally for a period of from 2 to 30 minutes e.g. about 15 minutes.

- 5 Low temperature firming treatment comprising heating to a temperature in the range 50 to 70°C is known to increase the firmness retention in vegetables on subsequent high temperature treatments such as cooking. It is known that pectin methyl esterase activity is increased by such a
- 10 heating stage and mediation of firming due to pectin demethylation appears to explain part of the observed increased firmness retention. The quality benefits of low temperature firming and conventional freezing are limited. However, the combination of low temperature firming and the
- 15 controlled freezing regime according to the invention provides a significant improvement. The vegetables are heated to a temperature in the range 50 to 70°C for a period of from 5 to 30 minutes, generally about 15 minutes.
- 20 The vegetables may be subjected to both the calcium and low temperature firming treatments in either order and simultaneously e.g. by immersing in calcium solution at ambient followed by immersing in calcium solution at 65°C and optionally immersing again in calcium solution at
- 25 ambient temperature.

The controlled freezing regime comprises undercooling to a maximum core temperature of less than or equal to -5°C and reducing the core temperature to less than or equal to -

30 18°C.

Under-cooling 'the core' of the vegetable or part thereof to a maximum temperature of less than or equal to -5°C ensures that enough heat has been removed from the material to allow rapid and uniform ice formation in the freezing step (iii) and thereby provide a significant reduction in extracellular ice formation. Preferably the vegetable or part thereof is under-cooled to a temperature from -5 to -15°C , most preferably from -7 to -12°C . It has been shown that merely reducing the core to -1 or -2°C without further under-cooling is not sufficient for the rapid initiation of freezing needed for the desired reduction in extracellular ice and consequent product benefit.

In order to under-cool effectively, without initiating ice crystal formation, the temperature difference between the centre of the core and the surface of the vegetable or part thereof must be kept to a minimum.

It has been shown that temperature differences between core and surface at the point of initiation of ice formation can vary significantly with conventional approaches to freezing. With the conventional blast freezing, when the surface of the vegetable material reaches 0°C and ice formation starts, the core is much warmer and the initiation of ice formation in this region starts much later.

Conventional wisdom accepts that the quicker the temperature drops during freezing, the more rapidly freezing occurs and the more favourable the vegetable properties achieved. Commercial preparation of frozen vegetables has therefore sought to speed up the cooling rates of commercial freezing equipment. It is counter intuitive and therefore surprising

to now find that where the rate of cooling is slowed to achieve a defined level of under-cooling within the vegetable core initiation of freezing can be induced throughout a product almost instantaneously.

5

In accordance with the present invention there is provided a process therein the rate of cooling is slowed sufficiently to achieve only a small temperature difference between core and surface and thereby induce under-cooling at the core of the vegetable material to a maximum temperature of less than or equal to -5°C . Ice formation with further temperature reduction can then occur throughout the vegetable material at approximately the same time. This has been found to result in a higher proportion of ice crystal formation within the cell structures defined by the cell walls i.e. intracellular ice and more favourable vegetable properties when consumed.

The temperature difference between the core and surface, and also within the core itself is dependent on the rate of cooling of the vegetable material. Rate of cooling is in turn dependant on the size of the vegetable material to be frozen and the surface area that it exhibits. It is believed to be within the capability of the person skilled in the art to decide on an appropriate cooling rate to achieve under-cooling to maximum core temperature of less than or equal to -5°C for a vegetable of a particular size and surface area.

Sensory analysis has confirmed that both the appearance and the texture of vegetables prepared according to the present invention show improvement over the conventional freezing

methods known in the art and the results obtained closely resemble those for fresh unfrozen vegetables. In particular the firmness of vegetables according to the invention are significantly improved over frozen vegetables known in the art.

To ensure effective under-cooling it is preferred that the cooling rate utilised for the process of the invention maintains maximum and minimum temperatures between the surface and the core within 6°C of each other, preferably less than or equal to 3°C, most preferably less than 1.5°C of each other e.g. two temperature probes are inserted into the vegetable e.g. a potato which is being cooled according to the invention, the first at 10mm from the surface of a potato tuber and the second in the centre of the tuber; when the first probe detects a temperature of 0°C the second should read less than or equal to +6°C, preferably less than or equal to +3°C, most preferably less than +1.5°C.

Preferably the vegetable material will be cooled in a blast freezer wherein the freezer set-point is progressively reduced according to the following regime:

55-65 minutes at 0°C
25 25-35 minutes at -5°C
10-20 minutes at -10°C
10-20 minutes at -12.5°C
70+ minutes at -30°C

Most preferably the vegetable material will be frozen in a blast freezer wherein the freezer set-point is reduced according to the following regime:

60-70 minutes at -12°C downwards airflow about 1 m/s

25-35 minutes at -30°C downwards airflow about 4.5 m/s

- 5 The temperature at which initiation of freezing occurs in step (iii) will depend on the nature of the vegetable that is being subjected to this freezing process, the rate at which cooling continues below -5°C as well as the presence or absence of nucleating agents. Initiation of freezing may
- 10 occur at any point when the temperature within the core is at a maximum of less than -5°C . Typically initiation of freezing will occur when the temperature within the core is at a maximum temperature of from -7°C to -12°C .
- 15 In one embodiment of the process at least 40% of ice formation within the core of said vegetable or part thereof in step (iii) occurs within a plurality of cellular structures, wherein the perimeter of each cellular structure is defined by a cell wall. Preferably at least 60 % of said
- 20 ice formation occurs within said plurality of cellular structures, more preferably 80%. Most preferably 90% of ice formation at the core of said vegetable or part thereof occurs within said plurality of cellular structures.
- 25 In a vegetable prepared according to the present invention it is preferred that at least 60% of said ice formation occurs within said plurality of cellular structures, more preferably 80%. In a most preferred embodiment 90% of ice formation at the core of said vegetable or part thereof
- 30 occurs within said plurality of cellular structures as these

vegetables most closely resemble the appearance and texture of fresh vegetables.

5 The effect of extra-cellular ice formation on the cellular structure of the vegetable material has been demonstrated, wherein the cavitation in thawed vegetables caused by extra-cellular ice growth has been quantitatively evaluated.

10 Measurements have been carried out to demonstrate the differences in the disruption of the cellular structures in thawed vegetables between conventional freezing and freezing by a process of the invention.

15 Fixation Method: The tissue pieces were received already thawed. They were transferred to fixative, formol-acetic alcohol (FAA) at room temperature and left to fix for not less than 72 hours.

20 Embedding & Sectioning: After fixation, the tissue pieces were dehydrated and embedded in paraffin wax. They were then sectioned to a nominal thickness of 5 μ m, and mounted on glass slides.

25 Sections were cut through the tissue pieces which had been subjected to the different freezing treatments. Three images were selected from each section, two from opposite sides of the tissue section (avoiding tissue very close to the edge of the section) and one image from near the middle. Care was taken to ensure that there was no overlap between
30 the fields.

For image enhancement the images were first converted to B/W (18-Bit) format and image contrast was greatly increased by

carrying out a 100 pixel value downfield shift of the entire image, followed by re-ranging it back to its full dynamic range (pixel value range 0 - 255). This left the cell walls a very dark grey and remainder of the image a very light grey.

The ice cavities were identified by eye from their morphology. Using the 'magic wand' range selector, set to a tolerance of ± 15 , with the contiguity control switched on, the cavities were selected manually and filled with white (pixel value = 255). The remainder of the image was rendered black (pixel value = 0).

Measurements were done on a Kontron KS300 image analyser. The total number of pixels in the ice cavities were counted (measured as a filled area - i.e. treating any small inclusions within the cavities as if they were not there), added together and expressed as a percentage of the pixels in the entire image.

For the purpose of the present invention a vegetable or part thereof may be selected from the group comprising potato, swede, turnip, pumpkin, onion, broccoli, tomato, zucchini, aubergine, water chestnut, pepper, mushroom, peas, carrot, spinach, sugar-snap peas, green bean and mange-tout. Most preferably said vegetable or part thereof is tomato.

Vegetable or parts thereof according to the present invention can be readily used in a variety of commercial catering or domestic frozen food products. In particular vegetables of the present invention are ideally suited to frozen ready prepared meals where their superior texture

considerably improves the product quality. Therefore a further aspect of the invention relates to the use of a vegetable of part thereof as described above in a frozen meal.

5

Description of the Drawings

Figures 1 to 3 represent plots of force (N) against displacement (mm) obtained from compressive mechanical tests
10 conducted on samples from Examples 1 to 3 respectively, and

Figures 4 to 7 represent low temperature scanning electron microscope images conducted on samples from Example 3.

15 The invention will be illustrated by the following Examples in which the following techniques were employed:

Tomato Freezing Method (Controlled Cooling)

The freezing method used a Montford Environment Test
20 Chamber. This programmable piece of apparatus is capable of producing very finely controlled temperature gradients in a reproducible manner. The programme used gives rise to a linear gradient down from +10° to -30°C over 16 hours. The tomatoes were transferred to the chamber and then frozen
25 using the 16 hour gradient programme.

Compressive Mechanical Tests of Tomatoes

The mechanical plots show typical compressive mechanical
30 tests on pieces of tomato cut from the outer pericarp of several fruits. The pieces were either frozen raw or initially heated and/or immersed in calcium solution as

described by the invention, prior to being frozen by the process of the invention or by conventional blast freezing. After freezing, the pieces were thawed by immersion in ambient water. For each regime, ten pieces were tested and
5 a typical force-displacement plot was chosen to represent each regime.

For the purposes of the mechanical tests, 1cm diameter cylinders of tissue were cut from the pericarp of the tomato
10 using a corkborer. These pieces were processed as described previously. The tissue cylinder was then compressed with a flat plate to about 70-80% strain at a crosshead speed of 2400mm/min using a Dartec Series HC10 Servo-Hydraulic Testing System.

15

Tomato Cooking

Cooking was conducted on tomato portions (whole tomatoes cut into 4 to 6 portions while still frozen). The portions were cooked by frying in oil until they reached a temperature of
20 at least 70°C.

Example 1

The following tests were conducted:

25 a) Calcium firming and controlled cooling (Ca/CC)

Tomato pieces were immersed in 1% calcium chloride solution for 15 mins followed by freezing by Controlled Cooling(CC). Tomato pieces were then cooked from frozen. Intact pieces apparent with skin still attached, minimal fluid released
30 and a firm texture in-mouth and to fork.

b) No firming treatment and controlled cooling (Raw/CC)

Raw tomato pieces were frozen by controlled cooling. Tomato pieces were cooked from frozen. The cooked tomato pieces were very soft, wet, lots of fluid lost and skin coming away from flesh.

5

c) No firming treatment and conventionally frozen (Raw/blast)

Raw tomato pieces were frozen in a conventional blast freezer set to -30°C throughout the freezing process.

10

Tomato pieces were cooked from frozen. The cooked tomato pieces were similar to those of test b) (Raw/CC).

d) Calcium firming and conventionally frozen (Ca/blast)

15 Raw tomato pieces were immersed in 1% calcium chloride solution for 15 minutes followed by freezing in a conventional blast freezer set to -30°C throughout the freezing process.

20 Tomato pieces were cooked from frozen. The cooked tomato pieces were less intact than those from test a) and disintegrated with a fork.

Compressive Mechanical Tests

25 Compressive mechanical tests were conducted on thawed samples from tests a) (Ca/CC), b) (Raw/CC) and d) (Ca/blast). The results are reported in Figure 1.

It will be seen from Figure 1 that the strength (max force prior to failure) is greater for the thawed samples treated according to the invention (Ca/CC) than samples treated by
30 Raw/CC or Ca/blast. The initial gradient (stiffness) and area under curve prior to failure (energy to failure) are

also greater. These mechanical parameters are known to relate to the perceived in-mouth texture (firmness) of the tissue.

5

Example 2

The following tests were conducted:

a) Heating at 65°C and controlled cooling (65C/CC)

10 Tomato pieces were immersed in water at 65°C for 15 minutes followed by freezing by controlled cooling. Tomato pieces were cooked from frozen.

b) No firming treatment and controlled cooling (Raw/CC)

Test b) as in Example 1.

15

c) No firming treatment and conventionally frozen (Raw/blast)

Test c) as in Example 1.

20 d) Heating at 65°C and conventionally frozen (65C/blast)

Tomato pieces were immersed in water at 65°C for 15 minutes followed by freezing in a conventional blast freezer set to -30°C throughout the freezing process.

25

30

Tomato pieces were cooked from frozen. The results of the tests a) to d) are summarised in the following Table.

TEST	RESULT AFTER COOKING
c) Raw/blast	V. mushy/difficult to cut; Pericarp to paste
d) 65c/blast	Less mushy, but soft, watery
b) Raw/CC	Firmer, more structure in tomato; easier to cut
a) 65C/CC	Firmer to cut

5

Compressive Mechanical Tests

Compressive mechanical tests were conducted on thawed samples from tests a), b) and c). The results are reported in Figure 2.

10

It will be observed from Figure 2 that the strength of the samples treated in accordance with the invention (65C/CC) is superior to the other samples.

15

Example 3

The following tests were conducted:

20

a) Calcium and low temperature firming and controlled cooling (Ca 65C/CC)

25

Tomato pieces were immersed in 1% calcium chloride solution at ambient temperature for 5 minutes, followed by immersion in 1% calcium chloride solution at 65°C for 5 minutes followed by immersion in 1% calcium chloride solution at ambient temperature for 5 minutes.

Thereafter the tomato pieces were frozen by controlled cooling.

Tests b), and c) were repeated as in Example 2. Test d) was the same as Test a) above, except that blast freezing was used instead of controlled cooling.

Compressive Mechanical Tests

Compressive mechanical tests were conducted on thawed samples from test a) and compared to thawed samples from b) untreated/ controlled cooled (Raw/CC), c) untreated/conventionally frozen (Raw/blast) and d) calcium firming/conventionally frozen (Ca/blast). The results are reported in Figure 3.

It will be observed from Figure 3 that the strength of the samples treated in accordance with the invention (Ca65C/CC) is superior to the other samples. The initial gradient (stiffness) and area under the curve prior to failure (energy to failure) are also greater.

Preparation of frozen tomato for quantitative evaluation of intra-cellular and extra-cellular ice content using low temperature scanning electron microscopy (LTSEM)

Frozen tomato samples in sealed polythene bags that had been stored at -80°C were kept cold by transferring them to the Scanning electron microscopy laboratory in an insulated box containing carbon dioxide.

Approximately 5mm x 5mm x 10mm sub-samples were cut 10mm from the outer edge of each sample using a liquid nitrogen

- pre-cooled scalpel blade. Cutting was carried out on an Aluminium plate sitting on a bed of solid carbon dioxide to maintain sample temperature. Sub-samples were mounted on to a 7mm conical depression in a 10mm diameter Aluminium scanning electron microscope stub using TissueTek compound at the point of freezing and immediately plunged in to Nitrogen slush. The stub + sample was mounted on to a holder and transferred to an Oxford Instruments CP2000 low temperature preparation chamber pumped with an Edwards 306 vacuum station (5×10^{-7} Torr) via an airlock. The sample was allowed to warm to -95°C and fractured using the point of a scalpel blade. After etching the ice for 5 minutes the sample was cooled to -110°C and coated with Gold/Palladium (6mA, 6×10^{-1} mBar Argon, 20 seconds). The vacuum was allowed to recover to 5×10^{-7} Torr and the sample transferred to a Cressington Instruments cold stage in a JEOL 6301F Low Temperature Field Emission Scanning Electron Microscope using an airlock transfer device.
- Samples were examined at -150°C and ice was identified as etched depressions in the fracture surface topography. Representative images of the intra and extracellular ice were recorded digitally at $\times 100$ and these images then quantified using a Zeiss (Imaging Associates) KS 400 Image Analysis system.

Figures 4 to 7 are LTSEM images for tomato samples subjected to Ca65C/CC, Raw/CC, Raw/blast and Ca65C/blast respectively.

- Figure 4 shows ice crystals within the cells and intact tissue structure. The tissue is firm when thawed.

Figure 5 shows large ice crystals, some in cells with some cells intact and damaged tissue.

Figure 6 shows large ice crystals with very damaged tissue structure. The tissue is soft and watery when thawed.

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Figure 7 also shows large ice crystals and very damaged tissue.

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Claims

- 5 1. A process for the production of a frozen vegetable or part thereof, wherein said process comprises the steps:

(i) subjecting a vegetable or part thereof to a firming treatment selected from:

- 10 a) immersing the vegetable or part thereof in a solution of a calcium salt.
b) heating the vegetable or part thereof to a temperature in the range 50 to 70°C, and
c) a combination of a) and b);

15

(ii) under-cooling to a core temperature of less than or equal to -5°C;

(iii) reducing the temperature to less than or equal to

20 -18°C.

2. A process as claimed in claim 1 in which the calcium salt is selected from calcium chloride, calcium sulphate, calcium citrate, calcium monophosphate and mixtures thereof.

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3. A process as claimed in claim 1 or claim 2 in which the solution of calcium salt comprised from 0.1 to 10% calcium.

- 30 4. A process as claimed in claim 3 in which the solution of calcium salt comprises about 1% calcium.

5. A process as claimed in any preceding claim in which the vegetable or part thereof is immersed in the solution of calcium salt for a period of from 2 to 30 minutes.

5 6. A process as claimed in any preceding claim in which the vegetable or part thereof is heated to a temperature of from 50 to 70°C for a period of from 2 to 30 minutes.

7. A process as claimed in claim 6 in which the
10 temperature is about 65°C.

8. A process as claimed in any preceding claim in which the firming treatment comprises immersing the vegetable or part thereof in a solution of calcium salt at ambient
15 temperature and immersing the vegetable or part thereof in an aqueous solution at a temperature of from 50 to 70°C (with or without calcium salt being present) in either order.

20 9. A process as claimed in claim 8 in which the firming treatment comprises the steps of:

immersing the vegetable or part thereof in a solution of calcium salt at ambient temperature for a period of from 2 to 30 minutes; thereafter

25 immersing the vegetable or part thereof in a solution of calcium salt at a temperature of from 50 to 70°C for a period of from 2 to 30 minutes, and

optionally immersing the vegetable as part thereof in a solution of calcium salt for a period of from 2 to 30
30 minutes.

10. A process according to any preceding claim wherein at least 40% of ice formation within the core of said vegetable or part thereof in step (iii) occurs within a plurality of cellular structures, wherein the perimeter of each cellular structure is defined by a cell wall.

11. A process according to any preceding claim wherein said vegetable or part thereof is selected from the group comprising potato, swede, turnip, pumpkin, onion, broccoli, tomato, zucchini, aubergine, water chestnut, pepper, mushroom, peas, sugar-snap peas, spinach, green beans, carrot and mange tout.

12. A process according to any preceding claim wherein said vegetable or part thereof is tomato.

13. A frozen vegetable obtained by a process as claimed in any preceding claim.

14. A frozen meal comprising a vegetable or part thereof as claimed in claim 13.

15. Use of a vegetables as claimed in claim 13 in a frozen meal.

AbstractFreezing Vegetables

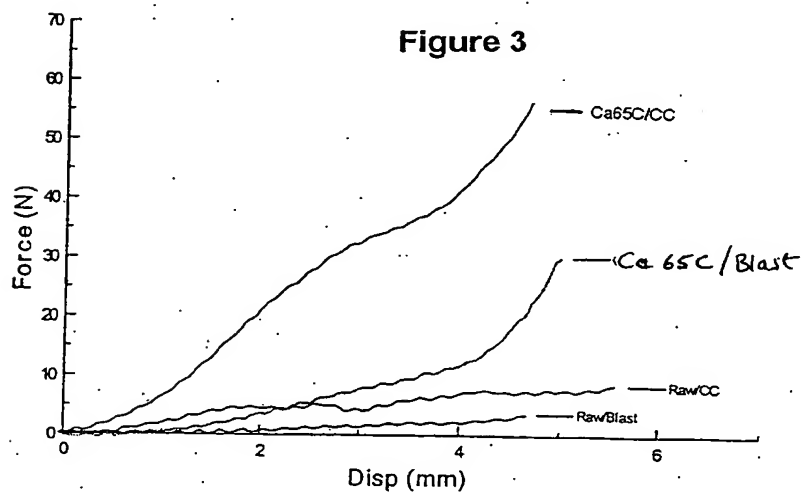
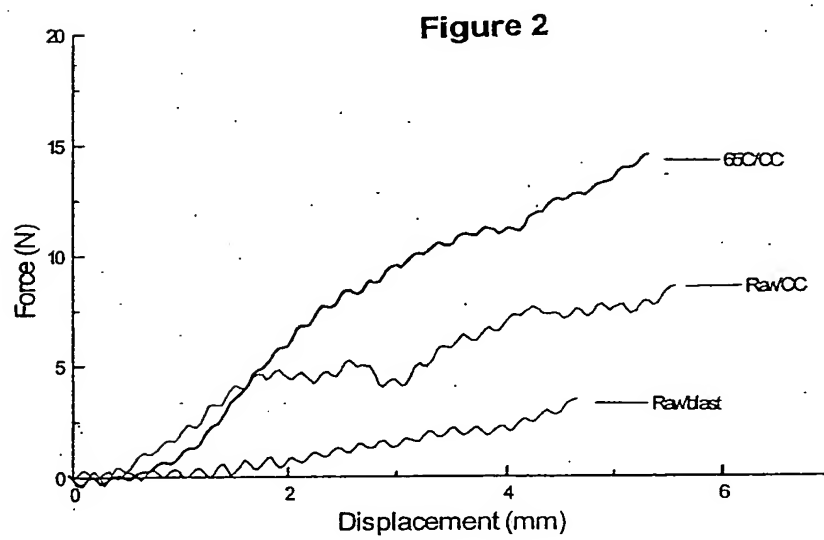
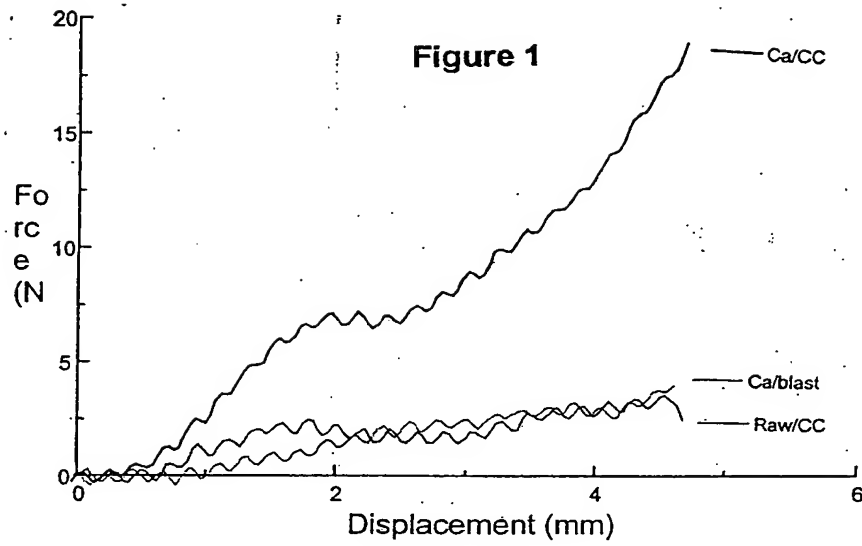
The present invention relates to a process for the
5 production of a frozen vegetable or part thereof, wherein
said process comprises the steps:

(i) subjecting a vegetable or part thereof to a firming
treatment selected from:

- 10 a) immersing the vegetable or part thereof in a
 solution of a calcium salt.
 b) heating the vegetable or part thereof to a
 temperature in the range 50 to 70°C, and
 c) a combination of a) and b);

15 (ii) under-cooling to a core temperature of less than or
equal to -5°C;

 (iii) reducing the temperature to less than or equal to
20 -18°C.



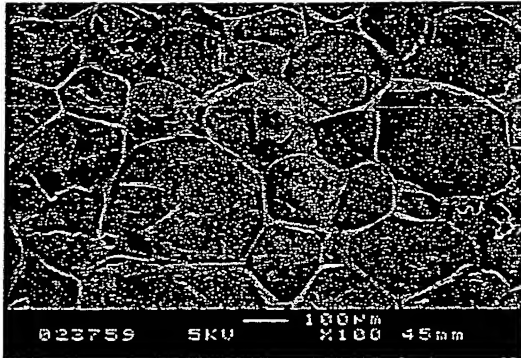


Figure 4

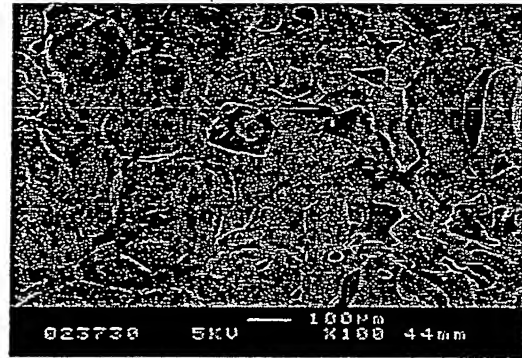


Figure 5

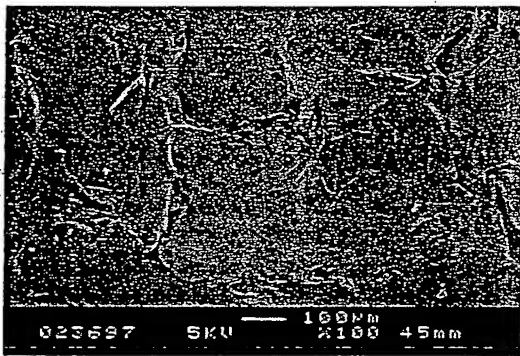


Figure 6

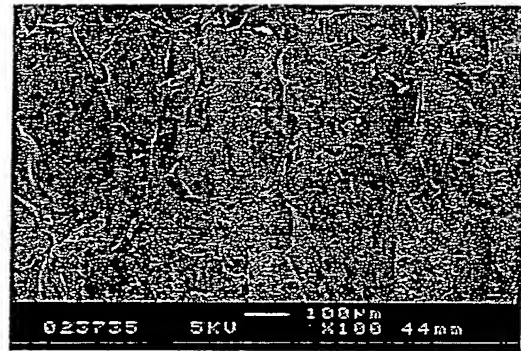


Figure 7

